Life Studies of Metal Films on Beta"-Alumina at High Temperature

Roger M. Williams, Adam Kisor, Brad Fiebig,
Roger Cortez, Margaret A. Ryan, Virgil Shields,
and Margie Homer

M.S. 303-308
Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Drive, Pasadena,
CA 91109
818 354 2727
rmw@.jpl.nasa.gov

Life Studies of Metal Films on Beta"-Alumina at High Temperature

Introduction

Applications of metallic films on sodium beta"-alumina solid electrolyte (BASE) ceramic in technology for the alkali metal thermal to electric converter (AMTEC) include both electrode and metallization functions.

Electrochemical characterization over the course of accelerated tests at up to 1173K for 6000 hours have demonstrated the durability of the best AMTEC elctrodes, such as tungsten-rhodium alloys.

The metallization of BASE for other purposes usually involves formation of a seal between BASE and a structural metal or ceramic component.

Characterization of metallizations using the same electrrochemical techniques should provide information about any degradation processes going on at the BASE/metal interface.

Life Studies of Metal Films on Beta"-Alumina at High Temperature

The Exchange Current

B is a semi-empirical constant equal to the exchange current of an AMTEC electrode corrected to unit activity sodium gas, and normalized for the collision rate of sodium atoms at the surface. Experimentally, this constant fits the exchange current well for temperatures over 700-1200K.

A fundamental model for the exchange current at Mo electrodes shows that B should give a good, but not perfect, fit to the exchange current from 600-1350K

B is usually measured at an AMTEC cathode in low pressure to moderate pressure sodium gas, in an AMTEC cell with an anode in high pressure sodium gas or liquid sodium. The anode at high activity sodium has negligible impedance.

Impedance spectra taken at a series of d.c. biases in AMTEC cells are best used to determine the exchange current, however AMTEC current-voltage curves may be used if other electrode parameters are known. It may also be determined from impedance spectra plus current-voltage curves taken in sodium exposure test cells, where both electrodes are at the same pressure.

JPL

Life Studies of Metal Films on Beta"-Alumina at High Temperature

The Electrolytic Cell Capacitance

The electrolytic cell capacitance will be proportional to the area of the BASE / electrode interface, and inversely proportional to the thickness of any insulating gap betweeen the solid electrolyte and the electyrode.

Hence formation of an interfacial degradation layer which is an insulator will be easily observed in the electrolytic cell's capacitance, most easily determined from electrochemical impedance spectroscopy.

Formation of electrochemically active degradation layers may give rise to a very large pseudocapacitance characterized by a very large time constant.

Life Studies of Metal Films on Beta"-Alumina at High Temperature

The Electrolytic Cell Series Resistance

The electrolytic cell series resistance will be modified by any reaction or morphology change which changes the electrical conductivity of the electrode or the ionic conductivity of the solid electrolyte.

In particular, formation of a insulationg layer at the BASE /elctrolyte interface, such as occurs when Al2O3/Cr2O3 forms due to the reaction of BASE with chromium will lead to an extremc increase in the cell resistance.

When the reaction of BASE with a reative metal leads toan insulating product more distributed throughout the BASE volume, as in the case of its reaction with Mn, the cell series resistance will rise, but not so extremely.

Reaction of BASE with Ti or V, which may lead to electrically conducting and ionically conducting products, may be expected to be observable as some sytematic change in the series resistance and the cell capacitance.

Life Studies of Metal Films on Beta"-Alumina at High Temperature

Electrode	Average B	Range of B(T)	Data set size/quality
Molybdenum	120	50-175(700-1225K)	Large, Excellent, AMTEC EIS
Platinum/Tungsten	80	50-100(900-1200K)	Moderate, Good, AMTEC EIS
Rhodium/Tungsten	120	90-150(1100-1200K)	Small, Good, AMTEC EIS Large, Good, SETC EIS & iV
Titanium Nitride	60	30-90(1050-1123K)	Small,Good, AMTEC EIS Moderate,Good, SETC EIS & iV
$Na_2MoO_4/Na_2Mo_3O_6/Mo$	500	400-600(1100-1200K)	Small, Fair, AMTEC iV curves

Life Studies of Metal Films on Beta"-Alumina at High Temperature

Mechanistic Distinctions

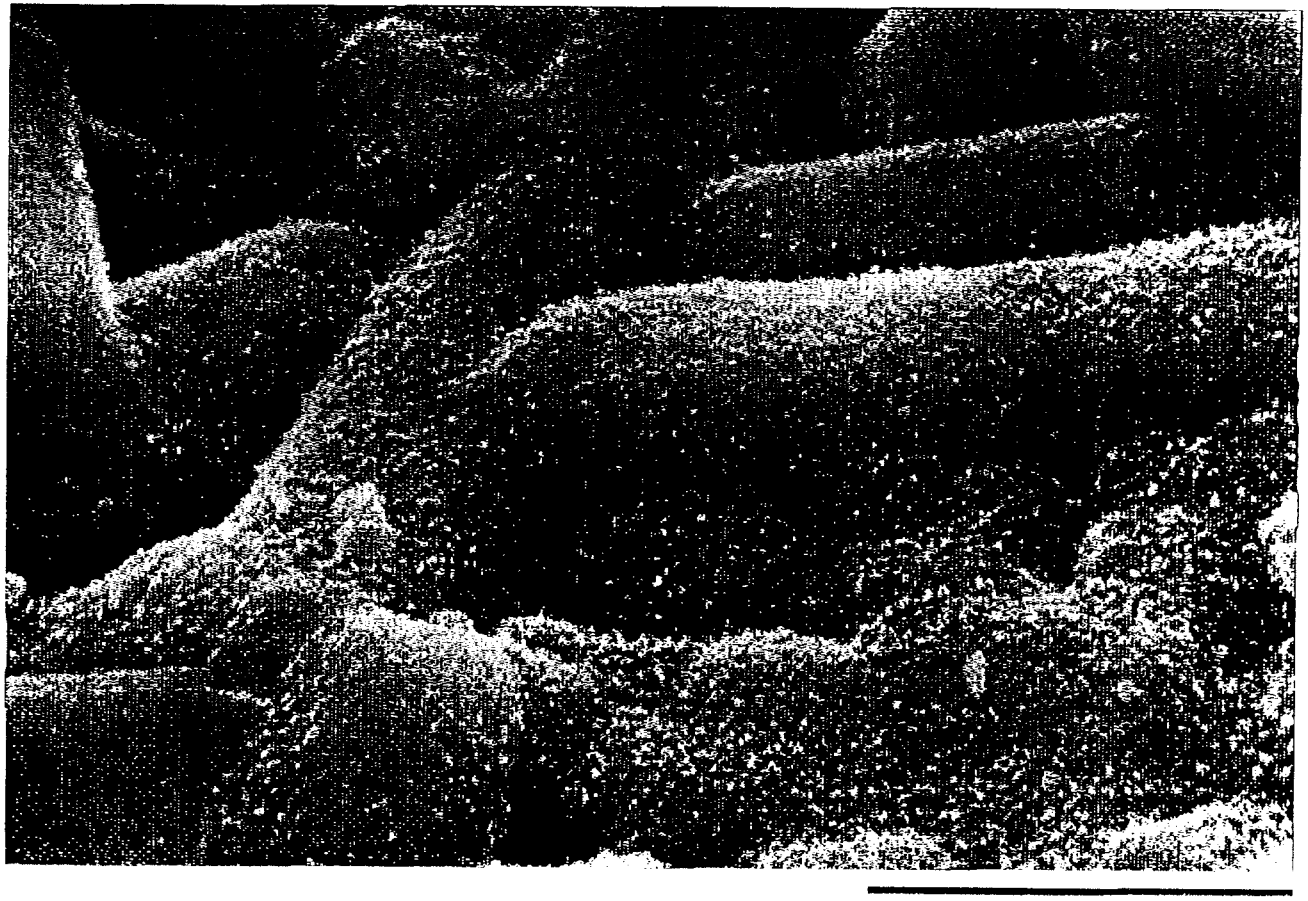
There is little evidence available to suggest that platinum/tungsten and rhodium/tungsten electrodes have a significantly different charge transfer mechanism than molybdenum electrodes.

Titanium nitride electrodes on sodium beta"-alumina solid electrolyte show an alteration zone (circa micron thickness) of gray to black material at the electrode/electrolyte interface. This material contains Ti, Al, O, and Na by XPS, but is poorer in Na than the solid electrolyte. Sodium ion transport through may add an activated step or reduce effective charge transfer reaction area.

While the accuracy of the high exchange currents measured for **$Na_2MoO_4/Na_2Mo_3O_6/Mo$** electrodes is not high, it is clear that they are much better charge transfer electrodes. We propose that charge transfer occurs at the exterior surface of the electrode over a much larger reaction zone; specifically on Mo grains coated with Na_2MoO_4 and at the surface of all $Na_2Mo_3O_6$ grains.

Life Studies of Metal Films on Beta"-Alumina at High Temperature

Surface Morphology of Na2MoO4/Na2Mo3O6/Mo AMTEC Electrode



10 microns

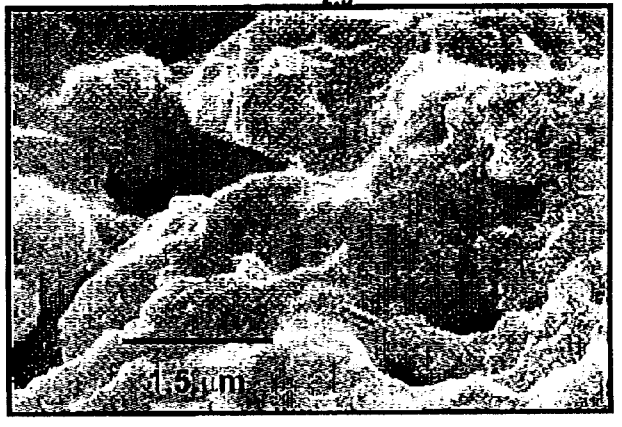
Life Studies of Metal Films on Beta"-Alumina at High Temperature

AMTEC Electrodes

TiN

1800 hrs/ 1170 K / Na_v / Ti lined

$Rh_{2.5}W$

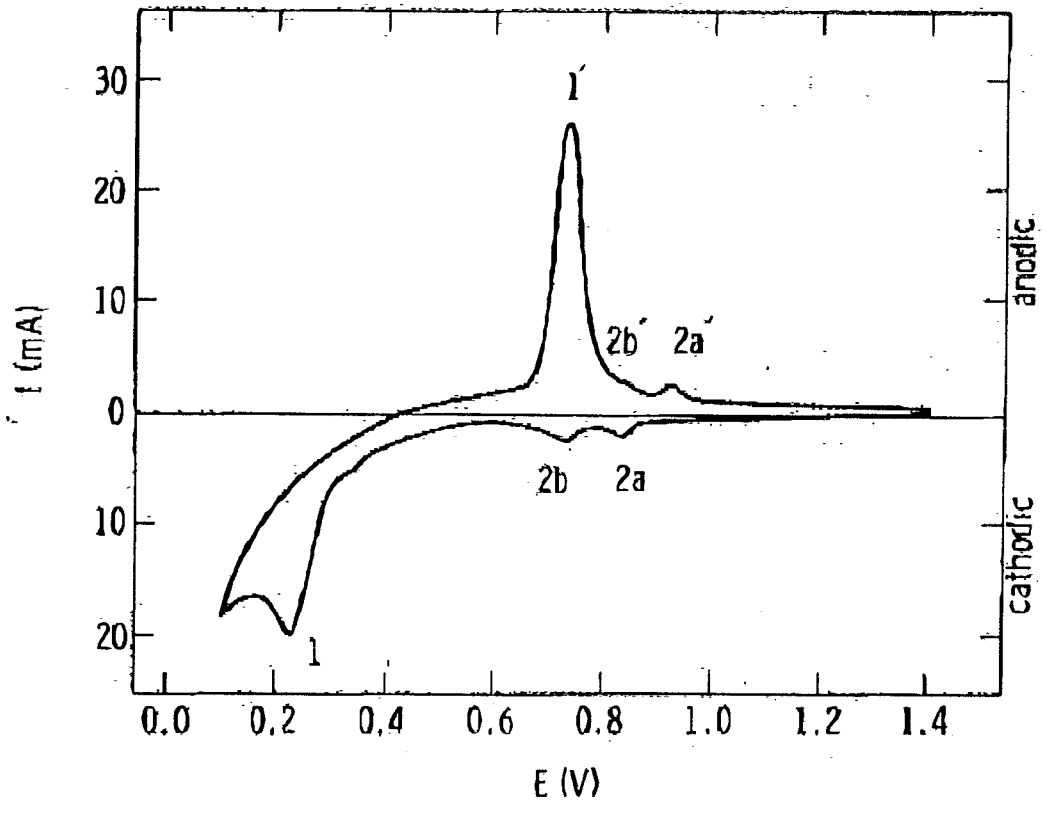


3000 hrs/ 1170 K / Na_v / Nb1%Zr lined

Mo

350 hrs/ 1100 K / Na_v

Life Studies of Metal Films on Beta"-Alumina at High Temperature



Cyclic voltammogram of a slightly oxidized Mo electrode in an AMTEC cell at 627K, scan rate 10 mV/sec, potential vs liquid sodium/sodium beta" alumina counter electrode, with iR losses small but not compensated. Williams et. al. JECS pp 2253, 133:11, (1986)

Life Studies of Metal Films on Beta"-Alumina at High Temperature

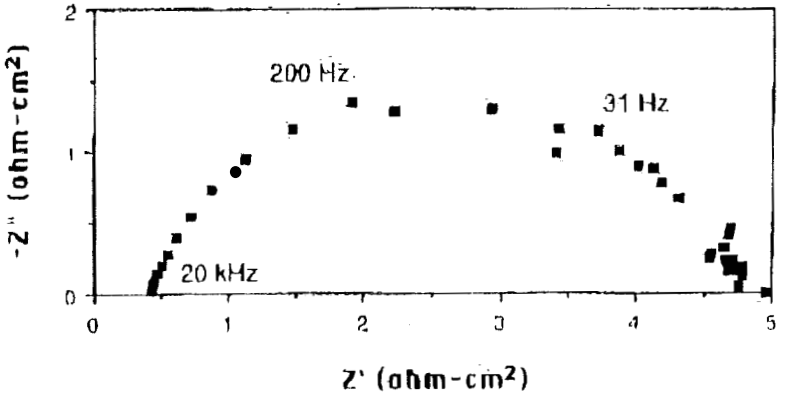


Fig. 7. AC impedance data for typical untreated W electrode, E8C, 1.00V, 1093 K.

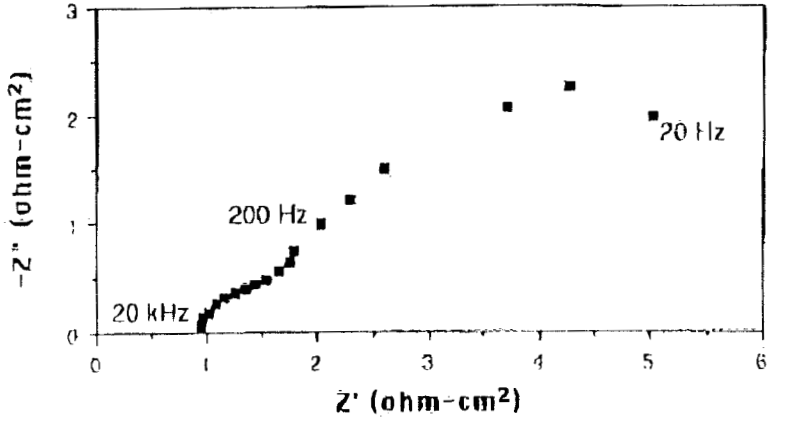
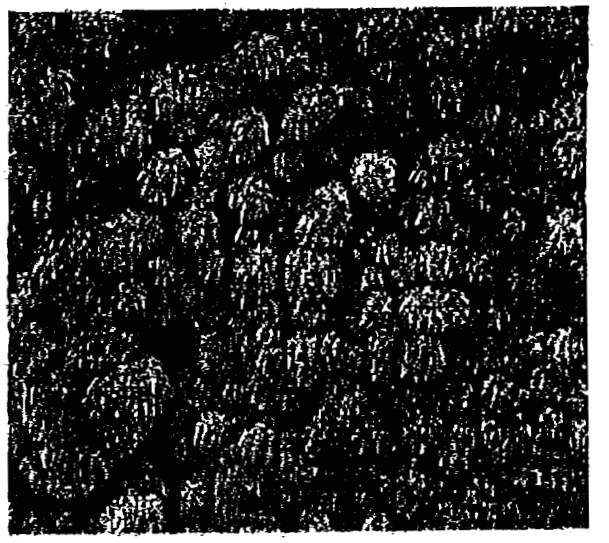


Fig. 8. AC impedance data for Na_2WO_4/W electrode, E1CT, 1.00V, 1048 K.



Life Studies of Metal Films on Beta"-Alumina at High Temperature

Conclusions

Mo and W as well as W/Rh and W/Pt alloys are unreactive toward the BASE surace for up to 4000 hours at up to 1173K in low pressure sodium vapor.

Ti alloys result in some degradation of the BASE surface, with inclusion of Ti, and both Cr and Mn lead to decomposition of BASE with formation of Cr_2O_3 and $MnAl_2O_4$ as well as Al_2O_3.